

- II. "The Latent Heat of Evaporation of Water." By E. H. GRIFFITHS, M.A., Sidney Sussex College, Cambridge. Communicated by R. T. GLAZEBROOK, F.R.S. Received December 28, 1894.

(Abstract.)

Section I.

Although the enquiry described in the paper,* of which this communication is an abstract, has engaged my attention for the last two years, the actual experiments on which the conclusions are based were not performed until the months of September and October, 1894. Many difficulties in the construction of the apparatus had to be overcome, also the necessary standardisation of the instruments occupied my leisure time for some months.†

The apparatus was designed so as to enable me to perform experiments at temperatures from 10° to 60° C., and I hoped to carry out my investigations over that range. Owing, however, to incidents described in Paper L, I have been able to complete the enquiry at two temperatures only, although a number of less satisfactory experiments, performed in a different manner from that finally adopted, give approximate determinations at other temperatures.

The apparatus is, I regret to say, of a very complicated nature, owing, in a great measure, to my desire to avoid observational errors by as far as possible so arranging the machinery as to make it self-recording and self-regulating. I do not, therefore, feel it possible to convey any clear idea of it in this abstract, and will confine myself to a short description of the method, and the communication of the conclusions to which the experiments have led me.

The calorimeter was suspended by glass tubes in a chamber, the walls of which were maintained at a constant temperature (θ_0). The methods by which θ_0 was kept constant have been fully described in a previous paper.‡ Since the publication of that communication some additions have been made by which the apparatus has been so improved that it may be regarded as almost perfect in its action over the range 10° to 60° .

A silver flask which contained the water to be evaporated was placed within the calorimeter, and the whole of the calorimeter exterior to the flask was filled originally with aniline, and afterwards with a

* Referred to in this abstract as "Paper L."

† Throughout this enquiry I have been assisted by Mr. C. Green, Scholar of Sidney Sussex College, Cambridge, to whom I return my sincere thanks.

‡ "The Mechanical Equivalent." 'Phil. Trans.,' 184 (1893), A, pp. 361—504.

singularly limpid oil, consisting of hydrocarbons only. This oil was stirred by paddles revolving about 320 times per minute. Within the oil was a platinum-silver coil whose ends were kept at a known potential difference when an experiment was proceeding. The supply of heat was balanced by the loss due to evaporation in the flask, and thus the temperature of the calorimeter (θ_1) was kept practically constant and equal to θ_0 throughout an experiment. True θ_1 oscillated slightly about θ_0 , but $\theta_1 - \theta_0$ rarely attained to 0.05° C. in experiments lasting 70 or 80 minutes, and the oscillations could be so controlled that $\theta_1 - \theta_0$ was alternately positive and negative. The advantages of the above method are that the results are not appreciably affected by—

- (1.) Errors in thermometry.
- (2.) Changes in the specific heat of water.
- (3.) The capacity for heat of the calorimeter.
- (4.) Loss or gain by convection, &c.

Had the calorimeter been filled with water, its capacity for heat would have been so great that a considerable loss or gain of heat might have caused but small change in θ_1 , hence the employment of the oil, above referred to, whose specific heat and specific gravity were both small, and thus its "volume heat" was only about four-tenths that of water. It was necessary to detect, and in some cases to measure, very small differences between θ_0 and θ_1 , and this was done by the use of differential platinum thermometers. A full description of these thermometers has recently been published.* Extremely minute differences of temperature could not only be detected, but also be measured by means of the arrangement adopted. In Paper L I describe the experimental proofs of the following statement: "It follows that the differences of temperature could be determined to 0.0004° C., and I am confident that differences of 0.0001° C. could be detected."

Had it been possible to secure (a) that θ_0 should remain absolutely unchanged; (b) that the value of $\theta_1 - \theta_0$ should be zero at the commencement and also at the end of an experiment, it would have been unnecessary to *measure* differences of temperature, since the variations during an experiment would, if the above conditions were observed, have no effect on the result. Let θ_1' and θ_1'' be the initial and final temperatures of the calorimeter, and C_{θ_1} the capacity for heat of the calorimeter and contents at the temperature θ_1 , then $C_{\theta_1}(\theta_1' - \theta_1'')$ gives the loss of heat of the calorimeter, and as I have shown that the loss or gain by radiation, &c., may be neglected, it follows that this heat was abstracted by the evaporation of some water. Also, if θ_0 varied, an additional correction had to be made. I have indicated

* "The Specific Heat of Aniline." 'Phil. Mag.,' January 1895.

by the expression Σq the supply of heat during an experiment due to the above sources.

A source of heat was the supply due to the stirring. Let thermal units per second due to this cause be Q_s , and let the stirring be maintained for a time t_s , then total mechanical supply = $Q_s t_s$. I have given full particulars of the manner in which the values of Q_s for different values of θ_1 were ascertained (Q_s increased as θ_1 diminished, owing to the increase in viscosity of the oil). A study of the results of the stirring experiments led to the following conclusion: "The values of Q_s given in the tables are certainly correct to better than 1 in 50 at temperatures 30° and 40° , for in no case do individual experiments (when reduced to the same rate) differ by 1 in 100. Now an error of 1 in 50 in Q_s would cause an error of only about 1 in 5000 in L . I am less certain, however, about the values of Q_s at 20° and 50° C."

The last, and by far the greatest source of heat, is the work done by the electric current. Let Q_e be the units per second due to this cause, and let the current be maintained for a time t_e .

Now
$$Q_e = \frac{e^2 n^2}{R_1 J} \dots\dots\dots (1),$$

where e is the potential difference of a Clark cell at 15° C., n the number of cells, and R_1 the resistance of the coil at temperature θ_1 , after the corrections for the rise in temperature of the wire due to the passage of the current, &c., have been made.*

Let m be the mass *in vacuo* of water evaporated.

Then
$$ML = Q_e t_e + Q_s t_s + \Sigma q \dots\dots\dots (2).$$

In order to give an idea of the comparative importance of the terms in equation (2), I give the *mean value* of each term resulting from the experiments.

Table I.

	$Q_e \times t_e.$	$Q_s \times t_s.$	$\Sigma q.$
When			
$\theta_1 = 40$ and $n = 4$	2150	19.2	± 1.6
$\theta_1 = 30$ and $n = 4$	2305	32.9	± 1.2
$\theta_1 = 30$ and $n = 3$	1752	32.9	± 1.2

* The value of J used in these reductions was 4.199×10^7 . If there is some error in the electrical standards, &c., by which I determined J , this is still the right value to use here, for the standards are the same, and the methods practically

There can be no question as to the accuracy with which Q_{ste} was measured. The term Q_{ste} is probably the one least accurately determined, but the probable error is not 1 in 100, and the quantity Σq was found to a far greater degree of accuracy than the above table shows to be necessary, as it was certainly known to 1 in 1000.

I will not here attempt any proof of the above statements, full particulars being given elsewhere, nor do I propose to describe the mode of carrying out an experiment, as I find it impossible to sufficiently compress the account of the operations.

I performed a large number of experiments when the evaporation of the water was promoted by the passage of a gas. Extreme precautions were taken to dry the gas and to prevent any carrying of heat by it either to or from the calorimeter, but the results of these experiments cannot be called satisfactory, as the differences between individual experiments at the same temperature in extreme cases amounted to as much as 1 per cent. The following table gives the results:—

Table II.

No. of expts.	Mean Temp.	L.
5	49·82	566·5
10	39·99	572·4
9	24·96	581·9

The rate of evaporation was greatly varied during these experiments, for the potential difference was changed from that of 1 to 3 Clark cells, hence the rate of evaporation was in some cases nine times as great as in others.

There is one curious coincidence, which, however, may be merely fortuitous. In two of these experiments nitrogen was passed through the water instead of air, and these two experiments give almost exactly the same value as my final results, viz. :—

Temp.	L (Nitrogen expts.).	L. Final values
24·96°	581·68	581·7
39·98°	572·72	572·7

The method finally adopted was that of allowing the water to fall drop by drop on to the interior surface of the silver flask, and causing identical, and it will be seen that any errors of this kind would be eliminated during the calculations. This remark, however, does not apply to Professor Schuster's correction for the specific heat of the air displaced, for we are not dealing here with differences in rate of rise caused by the displacement of air by water. His correction (1 in 4000) is therefore included in the above value.

it to boil off rapidly by sufficiently diminishing the pressure. The object of this arrangement was to ensure, as far as possible, that the temperature of the evaporating water was that of the flask (θ_1). Many precautions too numerous to be here referred to had to be taken before this method could be worked successfully, but when once the experimental difficulties had been overcome, the agreement between different experiments left little to be desired, and this continued to be the case although the conditions of the experiments were considerably altered. Different masses of water and different rates of evaporation gave closely concordant values of L .

Table of Results.

(An improvement was made in the apparatus after No. 5, and I attach greater weight to all succeeding experiments.)

Table III.

No. of expt.	Temp.	L.	No. of expt.	Temp.	L.
I	40·147°	573·11	XII	29·987	578·58
II	40·146	572·31	XIII	29·983	578·64
III	40·147	572·77	XIV	29·998	578·78
IV	40·144	572·61	XV	29·999	578·90
V	40·145	573·80	XVI	30·004	578·60
			XVII	29·993	578·83
VI	40·147	573·01	XVIII	29·993	578·60
VII	40·147	572·50			
VIII	40·147	573·00	Means	29·994	578·70
IX	40·149	572·28			
X	40·157	572·12			
XI	40·133	572·61			
Mean of all	40·146	572·74			
Mean of VI to XI	40·147	572·59			

I regret that the experiments are comparatively few in number, but they occupied so much time that I was unable to make further repetitions.

I do not, however, consider that such repetitions would have greatly strengthened the evidence, for the mean probable error of even a small group of experimental results like the above is less than the probable error of some of the constants involved in the reduction of those results.

For the reason previously stated I attach small value to Nos. I to V.

My conclusion therefore is—

Temp.	L.
40·15°	572·60
30·00	578·70

Section II.

On p. 218 will be found, I think, a fairly complete table of results published since the year 1843.

The values obtained by Winkelmann ('Wied. Ann.,' 9, 1880) are not included in the table, as they are not based on independent experiments, but deduced from the observations of Regnault.

In Paper L I have given reasons for my conclusion that much greater weight attaches to the values of Dieterici and Regnault than to those given by the other observers.

Dieterici's method was to determine the mass of ice formed by the evaporation of a certain mass of water at 0°. Hence, his results, like my own, are independent of thermometric errors, or errors in the determination of the water equivalent of his apparatus. Certain of his experiments were performed by placing the water to be evaporated in platinum, instead of glass, tubes, and to these he attaches, I think rightly, greater importance than he does to the remaining experiments. His conclusions are as follows:—

“Die Versuche mit dem Platingefässe ergeben

$$L = 596\cdot73,$$

mit einem wahrscheinlichen Fehler des Mittels von $\pm 0^\circ \cdot 13$.”*

He succeeded in altering the rate of evaporation very greatly, and that without affecting his results. I cannot here even enumerate other considerations which lead to the conclusion that the result of Dieterici's platinum tube experiments carries great weight.

As stated in the above table, Regnault performed twenty-two experiments over the temperature range -2° to $+16^\circ$. There can be little doubt, however, that his results over this range are of small value, and he was evidently of this opinion himself.†

Winkelmann has written a criticism of Regnault's experiments,‡ in which he comes to the conclusion that it is necessary to reject this series of experiments, and, in Paper L, I give additional reasons for their rejection. The chief arguments are as follows:—

- (1.) Regnault determined the temperature of the vapour in the spiral by observations of the *pressure* in the condenser.

* 'Wied. Ann.,' vol. 37, 1889, p. 504.

† See 'Mémoires de l'Acad.,' vol. 21, 1847, pp. 712—719.

‡ 'Wied. Ann.,' vol. 9, 1880.

Table IV.

Temperature.	Observer.	No. of expts.	Extreme values for L.	Mean L.	Reference.
0	Dieterici	20	595.52—598.84	596.8	'Wied. Ann.,' vol. 37, 1889.
-2 to +16	Regnault.	22	—	—	'Mémoire de l'Acad.,' vol. 21, 1847.
63 to 88	"	23	—	—	" " " "
99.88	"	44	533.3—538.4	536.67	" " " "
99.81	Favre and Silbermann ...	3	532.59—541.77	535.77	'Ann. de Chimie,' vol. 37, 1853.
100	Andrews	8	530.8—543.4	535.9	'Chem. Soc. Journ.,' 1849.
100	Berthelot	3	535.2—537.2	536.2	'Comptes Rendus,' vol. 85, 1877.
100	Schall	—	No details given	532.0	'Ber. d. Chem. Ges.,' vol. 17, 1884.
100.16	Hartog and Harker*	5	523.61—525.87	524.60	'Manchester Phil. Soc. Proc.,' 1893-94
119—194	Regnault	73	—	—	'Mémoire de l'Acad.,' vol. 21, 1847.

* It is right to add that Messrs. Hartog and Harker state that these are the results of "Preliminary Experiments," and should not be regarded as giving their final conclusions. I do not, therefore, include their work in my criticisms.

- This must have been (as Regnault himself points out) considerably below the pressure of the vapour in the flask.
- (2.) At low temperatures a small error in the pressure would cause a considerable error in temperature. For example, an error of 0.4 mm. in pressure would correspond (at 4° C.) to an error of 1° in θ .
 - (3.) All his observations of the change in temperature of the calorimeter at low temperatures were taken on a falling mercury thermometer, and an error of 0.01 (the limit to which he observed his thermometer) would change the resulting value of L by 1 in 500. Now, no observations on falling mercury thermometers can be relied on to give an accuracy of anything like the above order.
 - (4.) The extreme divergence between the results of these experiments would alone render them of small value.
 - (5.) Regnault's formula for the "total heat" ($606.5 + 0.305 \theta$) is not in agreement with his experimental results.

I have in my paper given further reasons for their rejection, but I think the above are alone sufficient to prove that at any rate the results of these experiments must be regarded with suspicion. I have also shown that the tendency of all the above sources of error is to make Regnault's values of L too high at these temperatures.

These above objections, however, lose all their force when applied to Regnault's determinations from 63° to 100°. His methods of experiment were entirely altered; for example, p was observed where the vapour was formed, and a large change in p would produce but a small change in θ . Also his thermometers were rising, the range of temperature was more than twice as great, and his results were far more uniform, &c.

At about 100° Regnault performed forty-four experiments, of which he rejects the first six as "preliminary"; the remaining thirty-eight give the following mean results:—

Temp.	"Total heat."
99.88	636.67

This would become 636.60 at 100°. Hence, if we assume that 1 gram of water in cooling from 100° to 0° gives out 100 thermal units, we get $L = 536.60$ at 100°.

Now, taking my values, viz.,

Temp.	L .
40.15°	572.60
30.00	578.70

We get

$$dL/d\theta = 0.6010.$$

If we assume with Regnault that L is a linear function of θ we can deduce the values at 0° and 100° , and we get 596.73 and 536.63 respectively.

Hence

Table V.

	Values of L .	
	0° .	100° .
Regnault	—	536.60
Dieterici	596.73	—
Griffiths (extrapolated)	596.73	536.63

I think that I am justified in calling this agreement remarkable, and there is evidence that it is not a mere coincidence.

Winkelmann, in his analysis of Regnault's work, states that the following formula gives the results of Regnault's experiments with greater accuracy than Regnault's own formula:—

$$L = 589.5 - 0.2972\theta - 0.0032147\theta^2 + 0.000008147\theta^3 \dots (W).$$

Now if we assume my value of $dL/d\theta$ we get

$$\text{“ Total heat ”} = 596.73 + 0.3990\theta \dots (G_2),$$

whereas Regnault's formula is,

$$\text{Total heat} = 606.5 + 0.305\theta \dots (R).$$

The following table gives in column III all Regnault's experimental results (R_e) below 100° , except those (below 63°) by his other mode of experiment, which I have given reasons for rejecting. Column VII shows the difference between R_e and the value given by formula (R). Column VIII gives $R_e - (W)$, and column IX $R_e - (G_2)$.

Table VI.

Comparison between Regnault's Experimental Results (R_e) over the range 63° to 88° , with the value given by formulæ (R), (W), and (G_2).

I. No. of expt.	II. Temp.	III. Experimental results (R_e).	VII. $R_e - R$.	VIII. $R_e - W$.	IX. $R_e - G_2$.
1	88.11°	633.4	0	+0.9	+1.5
2	87.83	633.1	-0.1	+0.8	+1.3
3	85.97	628.4	-4.3	-3.3	-2.6
4	85.24	628.6	-3.9	-2.9	-2.1
5	85.20	631.7	-0.8	+0.2	+1.0
6	84.68	629.9	-2.4	-1.3	-0.6
7	83.08	628.9	-2.9	-1.8	-1.0
8	82.66	631.0	-0.7	+0.4	+1.3
9	81.03	628.8	-2.4	-1.2	-0.3
10	80.60	627.7	-3.4	-2.2	-1.2
11	80.37	628.8	-2.2	-1.0	0.0
12	80.17	630.2	-0.7	+0.5	+1.5
13	79.55	630.1	-0.7	+0.7	+1.6
14	78.28	627.0	-3.3	-2.0	-1.0
15	76.50	628.6	-1.2	+0.3	+1.4
16	71.35	624.4	-3.8	-2.0	-0.8
17	71.11	622.2	-5.9	-4.1	-2.9
18	70.49	626.9	-1.1	+0.8	+2.0
19	69.70	626.4	-1.3	+0.7	+1.9
20	68.01	622.5	-4.8	-2.6	-1.4
21	66.30	624.7	-2.0	+0.2	+1.5
22	64.34	622.9	-3.2	-1.0	+0.5
23	63.02	625.5	-0.2	+2.3	+3.6
Sum of differences			-49.3	-17.6	+5.2
Mean difference			-2.14	-0.77	+0.23
If we omit Expt. 23 we get					
Sum of differences			-49.1	-19.9	+1.6
Mean difference			-2.23	-0.90	+0.07

We thus see that formula (G) gives a closer approximation to Regnault's experimental results over the above range than either of the other formulæ.

Again, the results of my earlier experiments, referred to above, lend support to formula (G).

One difficulty, however, presents itself. If there is any truth in the ordinarily accepted ratio of the "mean thermal unit from 100° to 0° " to the "thermal unit at 15° C.," then, so far from my own, Dieterici's, and Regnault's results being in agreement, they in reality differ considerably, for our values are expressed in different units. True, Regnault adopted the "thermal unit at 15° ," but, as his experi-

Table VII.

Temp.	L from pressure expts. (<i>supra</i>).	L. Formula (G).
25·0°	581·9	581·7
40·0	572·4	572·7
49·8	566·5	566·8

ments gave the "total heat," not the value of L, the results should be different after subtraction of the "total heat" of the water, for when subtracting we assumed the identity of the two units.

Dieterici adopted as the basis of his measurements the mass of mercury drawn into a Bunsen's calorimeter by the heat evolved from 1 gram of H₂O when cooling from 100° to 0°.* Now, according to Regnault,† the ratio of the "mean thermal unit" to the "thermal unit at 0° C." is as 1·005 : 1.

If we assume Rowland's, or Bartoli and Stracciati's, determination of the changes below 15° (my own have not extended below that temperature), we should get

$$\frac{\text{mean thermal unit}}{\text{thermal unit at } 15^{\circ}} = \frac{1\cdot005}{0\cdot994} \text{ approximately } = \frac{101\cdot1}{1},$$

and thus Dieterici's value of L at 0°, if expressed in terms of thermal unit at 15°, would become 603·3.

Again, according to Regnault we ought to subtract 100·5 from 635·60, and thus get L at 100° = 536·1.

The only reasonable explanation of this difficulty appears to me to be that the value of the "mean thermal unit" is practically the same as the value of the "thermal unit at 15° C."

I see nothing impossible in this supposition. As shown in Paper L, there is sufficient evidence that at low temperatures the capacity for heat of water decreases with rise of temperature. Rowland found a minimum indicated near 34°. If, therefore, the capacity for heat increases gradually above some such temperature, but more rapidly near 100°, it is quite conceivable that the "mean thermal unit" should closely approximate to the "thermal unit at 15° C." Our only experimental evidence to the contrary is that given by Regnault in his paper "De la Chaleur Spécifique." We know that his conclusions at low temperatures are incorrect, and I do not see that those at higher temperatures have greater value, for his methods of observation and experiment were in this case unaltered. The matter,

* 'Wied. Ann.,' vol. 37, 1889, p. 499.

† "De la Chaleur Spécifique." 'Acad. des Sciences,' tome xxi.

of course, can only be cleared up by a direct determination of the capacity for heat of water over the range 0° to 100° .

In Paper L, I give further evidence in support of the equality of the two units.

Considering the extreme attention which has been given during the last few years to the determination of the electrical units, it is strange that so little has been done regarding what is perhaps as important a unit, viz., that of heat. I venture to appeal to the Royal Society to take steps to place our knowledge in this respect on a firmer basis, and I would go so far as to express my belief that the method of measuring small differences of temperature described in Paper L, and also in the communication printed in the 'Philosophical Magazine' of this month, points out a way to the solution of some of the difficulties.

Section III.

The density of water-vapour at different pressures can be obtained from the thermodynamic equation $L = \frac{T}{J} (s' - s) \frac{dp}{dT}$. In Paper L, I have given the density at different pressures thus obtained by the substitution of my values of L and J .

We can also obtain what Winkelmann terms the "theoretical density" by assuming that water-vapour behaves as a perfect gas, having the same molecular weight. I have shown that if we take the most recent determinations of the atomic weight of oxygen,* the "theoretical density" of water-vapour at low pressures is almost identical with the density as deduced from the thermodynamic equation. At higher pressures (above 140 mm.) the density appears to remain nearly constant, and is about 1.02 times as great as the "theoretical density."

These conclusions are confirmed by a study of the "volume energy" of water-vapour at different temperatures.

Conclusion.

The results obtained by Dieterici at 0° C., by Regnault at temperatures 63° to 100° C., and by myself at intermediate temperatures, are represented with great accuracy by the formula

$$L = 596.73 - 0.6010 \theta.$$

* Scott, 'Phil. Trans.,' A, 1893, p. 507.